Imines and Derivatives. Part 23.[1] Anomalous ^{1}H NMR Spectrum of *N*-[1-(1-Naphthyl)ethylidene]-1-phenyl-2-propylamine: Conformation in Solution, Atropisomerism and an X-Ray Crystal Structure†

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^{1}H NMR spectra of the title imine in solution indicate the presence of three stereoisomers due to *E*/*Z* isomerism about the imino bond and atropisomerism about the 1-naphthyl imino bond in the *Z*-isomer. The most abundant *Z*-isomer, which was isolated in crystalline form, exhibits a highly unusual NMR signal at δ 5.9 assigned to a naphthyl proton α to the imino group. The X-ray crystal structure reveals that this hydrogen atom is situated only 2.7 Å above the face of the phenyl ring of the *N*-1-phenyl-2-propyl moiety and hence experiences a large diamagnetic ring current shielding effect. An attractive edge-to-face ring interaction involving this naphthyl proton and the π-electrons of the proximate phenyl group could account for this observation. The marked temperature dependence of this NMR signal is quantitatively analysed in terms of a fast equilibrium in solution between the conformation favoured in the solid state and a second conformation which lacks the ring current effect.

In the course of our investigations into imines and derivatives,[1] the title imine (**1**) was prepared from amphetamine (1-phenyl-2-propylamine) and 1-naphthylethanone and was subjected to routine chemical and spectroscopic analysis.

While microanalytical data and the IR [ν_{max} 1 645 cm^{-1} (C=N) in Nujol] and mass (M^+ at *m*/*z* 288, 11%) spectra were in accord with the expected structure, the ^{1}H NMR spectrum (Figure 1) appeared to be anomalous. An unexpected doublet signal was evident at δ 5.91 in deuteriochloroform solution, a region usually associated with vinylic protons. Additionally, two sets of alkyl resonances were observed in freshly prepared solutions, *viz.* methyl doublet signals at δ 1.11 (component **A**, 62%) and 1.05 (component **B**, 38%), and imino methyl singlet signals at δ 2.30 (**A**, 62%) and δ 2.33 (**B**, 38%). Furthermore, when the solution was allowed to stand for a few hours a third set (**C**) of signals developed at δ 1.38 (d), 2.00 (s), and 4.11 (m). After *ca.* 3 days at ambient temperature (20 °C) an equilibrium was attained at a component distribution **A**:**B**:**C** = 49:31:20% in deuteriochloroform solution.

^{13}C NMR spectra of (**1**), see the Experimental section, corroborated the above findings. A freshly prepared solution showed doubling of most carbon resonances, and on standing a third set of signals slowly developed. In particular, the equilibrated deuteriochloroform solution showed three imino ^{13}C=N signals at δ 167.1 (component **B**), 166.7 (**A**), and 166.3 (**C**). This observation, together with the absence of ^{13}C NMR signals attributable to a $=CH_2$ moiety, establishes that all three components of (**1**) are imines. Hence imine–enamine tautomerism[2] is not responsible for the multiplicity of signals.

More definitive structural information was obtained from an experiment in which a few crystals of imine (**1**) were dissolved in deuteriochloroform pre-cooled to −50 °C and then a 270 MHz ^{1}H NMR spectrum was quickly recorded at −50 °C. The resulting spectrum was essentially that of component **A** with only a trace contribution from component **B**.‡ The proportion of **B** increased to its equilibrium value when the sample tube was removed from the probe for a few minutes, allowed to warm to ambient temperature, and the spectrum recorded again at −50 °C. Subtraction of initial and equilibrated spectra, with appropriate weightings, provided individual spectra of components **A** and **B** (Figures 2 and 3).

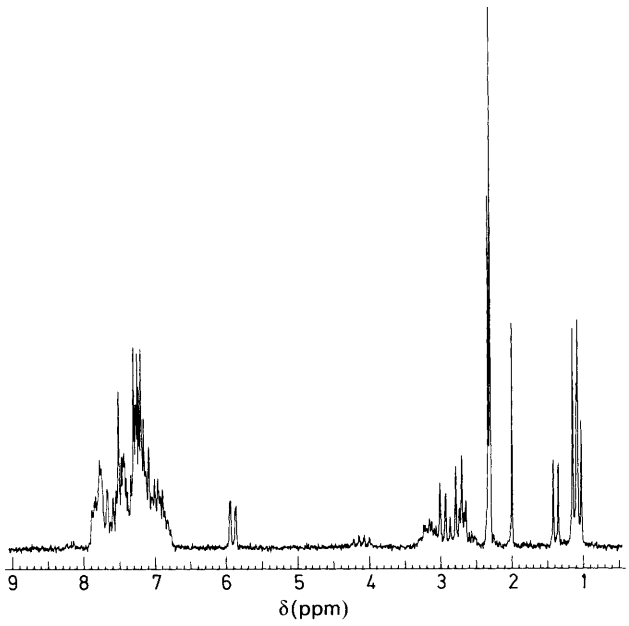
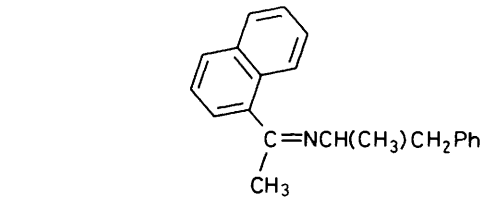


Figure 1. 90 MHz ^{1}H NMR spectrum of imine (**1**) recorded at 25 °C in deuteriochloroform after standing for 2 days to equilibrate.

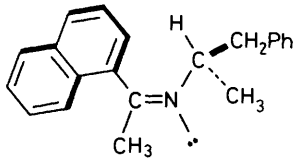
Both components **A** and **B** clearly have the same skeletal structure with CH*Me* doublet signals at δ 1.11 (^3J 6.0 Hz) and

† Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

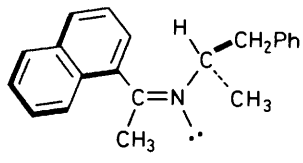
‡ The crystallization of isomer **A** from a pentane solution of imine (**1**) which consists of a three-component equilibrium mixture involves a second-order diastereoisomeric transformation. Thus as isomer **A** crystallizes out of the warm solution the equilibrium will be driven in favour of this component.



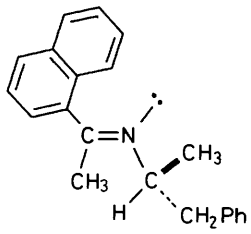
(1)



(1a)



(1b)



(1c)

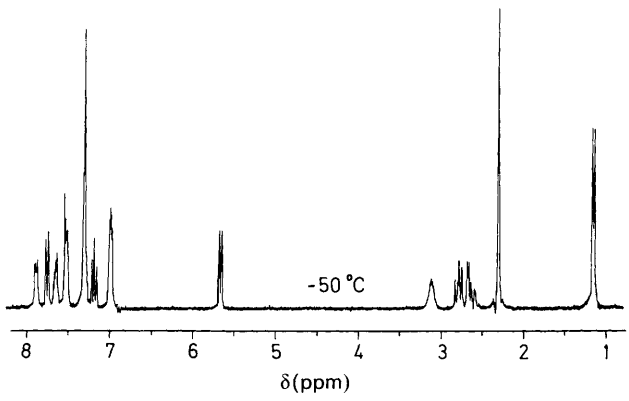


Figure 2. 270 MHz ^{1}H NMR spectrum of imine (**1**) recorded in deuteriochloroform at −50 °C following dissolution of the crystals at −50 °C. The signals of atropisomer (**1b**) have been removed by spectral subtraction.

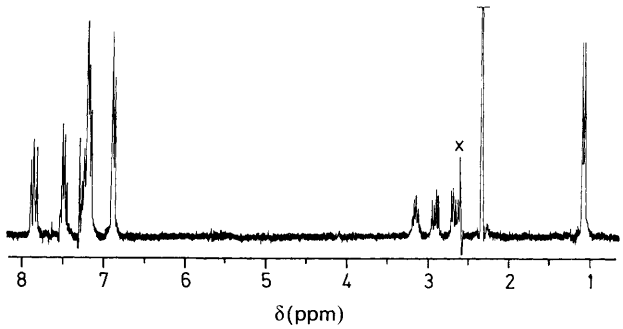


Figure 3. 270 MHz ^{1}H NMR difference spectrum obtained in deuteriochloroform at −50 °C, showing the spectrum of atropisomer (**1b**); peak labelled 'X' is a subtraction spike.

1.05 (^3J 6.2 Hz) respectively; complex C*H*Me multiplet signals at δ 3.11 and 3.14; singlet *Me*C= signals at δ 2.30 and 2.33; and complex naphthyl ring signals. Significantly the benzylic resonance of each component consisted of two AB subspectra centred at δ 2.71 and 2.79 respectively. Manual analysis of the AB section of these ABX spectra gave $^2J_{AB}$ 13.0 Hz, $^3J_{AX}$ *ca.* 8.9 Hz, and $^3J_{BX}$ *ca.* 4.1 Hz for component A, and $^2J_{AB}$ 13.1 Hz, $^3J_{AX}$ *ca.* 7.2 Hz, and $^3J_{BX}$ *ca.* 6.3 Hz for component B. This confirms the integrity of the amphetamino $PhCH_2CH$ moiety where the diastereotopic benzylic protons exhibit an AB part of an ABX system.* The CH (X) signal of both components is a complex multiplet owing to further coupling to the methyl group.

The ^{1}H NMR signals of components **A** and **B** are assigned to 1-naphthyl atropisomers (**1a**) and (**1b**) respectively of the imine in the *Z*-configuration. The 1-naphthyl moiety is twisted out of the imino plane and rotation is restricted by the proximate *cis* *N*-alkyl group. This leads to a chiral axis which in combination with the chiral *N*-1-phenyl-2-propyl centre gives rise to diastereoisomers **A** and **B**. Hindered rotation about 1-naphthyl imino bonds has been observed previously in related compounds[2–4] where a 1-naphthyl group is located *cis* to an *N*-alkyl group.

Subtraction of the 270 MHz ^{1}H NMR spectrum (recorded at ambient temperature in deuteriochloroform solution) of the rapidly equilibrated **A**/**B** component mixture from that of the fully equilibrated three component mixture, afforded a spectrum of the minor component (**C**). This difference spectrum confirmed the intact skeletal amphetamine imine structure of component **C** with signals at δ 1.38 (d, ^3J 6.2 Hz, CH*Me*), 2.00 (s, *Me*C=), 2.97 (AB part of ABX, $^2J_{AB}$ 13.1 Hz, $^3J_{AX}$ + $^3J_{BX}$ 13.1 Hz, CH_2Ph),† 4.11 (X multiplet which is split further by Me, CH) and 7.2–7.8 (complex, aromatic). Hence component **C**, which slowly develops on standing in solution at ambient temperature, is assigned to the *E*-imine (**1c**).* This assignment is supported by the 10 ppm upfield shift of the vinylic methyl carbon signal of component **C** in the ^{13}C NMR spectrum (Experimental section) relative to its position in components **A** and **B**. Assignment of the vinylic methyl ^{13}C signals was confirmed by observing that they essentially disappeared (due to deuteriation of the vinylic methyl protons[2]) when *ca.* 0.15 cm^3 of deuteriomethanol were added to the deuteriochloroform solution of the imine.

Previous work on related imines has established that an α-carbon situated *syn* to an *N*-alkyl group resonates 9–15 ppm upfield from an α-carbon situated *syn* to the imino nitrogen lone-pair electrons.[2,5] The relatively slow equilibration of components **A** and **B** with component **C** at ambient temperature also confirms that **C** rather than **B** is the *E*-imine (**1c**). Previous studies of related *N*-alkyl ketimines have established that *Z* ⟶ *E* isomerization occurs with a half-life of several hours at ambient temperature.[2,6] On the other hand, rotation

* The observation that the benzylic protons in components **A**–**C** give NMR signals appropriate to the AB part of an ABX system and that the CH resonance is a complex multiplet eliminates the possibility (suggested by a referee) that one of these components might be the structurally isomeric imine, $1\text{-}C_{10}H_7CH(Me)N{=}C(Me)CH_2Ph$. In any case, isomerization of this type usually requires a strong base to remove the NCH proton.

† One of the AB subspectra in this benzylic ABX system was a single line, hence the individual values of $^3J_{AX}$ and $^3J_{BX}$ could not be ascertained.

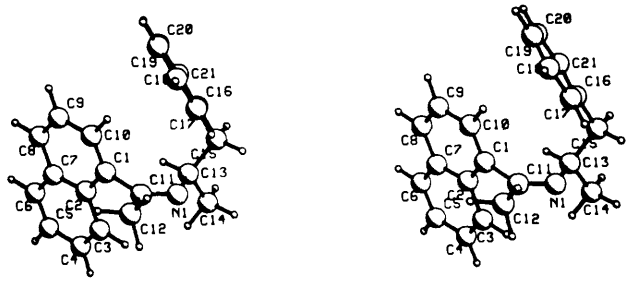


Figure 4. Stereoscopic view of the solid-state structure of imine (**1**) showing the crystallographic atom numbering.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with esds in parentheses.

Atom	*x*	*y*	*z*
N	536(5)	5 003(3)	2 949(3)
C(1)	2 910(6)	4 731(4)	4 040(4)
C(2)	3 521(6)	3 829(4)	4 077(3)
C(3)	3 291(7)	3 196(4)	3 310(4)
C(4)	3 893(8)	2 309(5)	3 364(5)
C(5)	4 753(10)	2 004(6)	4 136(5)
C(6)	5 002(8)	2 579(5)	4 861(6)
C(7)	4 383(7)	3 470(4)	4 819(4)
C(8)	4 621(7)	4 089(4)	5 587(4)
C(9)	3 995(7)	4 962(4)	5 534(3)
C(10)	3 151(7)	5 277(4)	4 765(3)
C(11)	2 085(7)	5 077(4)	3 181(3)
C(12)	3 260(8)	5 674(5)	2 633(4)
C(13)	−681(6)	4 494(4)	3 496(4)
C(14)	−1 476(9)	3 731(5)	2 948(5)
C(15)	−2 025(6)	5 187(4)	3 825(4)
C(16)	−1 306(7)	5 919(4)	4 424(5)
C(17)	−605(8)	6 726(4)	4 083(6)
C(18)	120(10)	7 382(6)	4 622(8)
C(19)	150(10)	7 257(7)	5 508(8)
C(20)	−506(10)	6 459(7)	5 884(6)
C(21)	−1 254(8)	5 791(5)	5 345(5)
H(10)	2 681	5 982	4 749

about 1-naphthyl–imine bonds takes place very rapidly at ambient temperature (though it is slow at −50 °C).[2] Thus the barrier to interconversion of atropisomers **A** and **B**, measured[7] from the dynamic coalescence of the amphetamino methyl doublet signals at 107 °C (270 MHz) in 1,2,4-trichlorobenzene–[$^2H_{10}$]-*p*-xylene (7:1), was determined to be $\Delta G^{\ddagger}_{B\rightarrow A}$ 20.5 ± 0.3 kcal mol^{-1}. This barrier is similar to barriers for rotation about 1-naphthyl–imine bonds in other *Z*-imines and is significantly less than the barriers to *E* ⟶ *Z* isomerization.[2,3,6]

The *E*-isomer (**1c**) does not show evidence of atropisomerism owing to fast rotation, on the NMR time-scale, of the much less sterically restricted 1-naphthyl moiety which is located *trans* to the bulky *N*-alkyl group and *cis* to the nitrogen lone-pair electrons.

Our principal interest in the ^{1}H NMR spectrum of imine (**1**) concerned the anomalous doublet signal at δ 5.91. Integration established that this signal was due to one proton of the major component **A**. It is far upfield of the region δ 7–8 normally associated with naphthyl ring protons. The direction of the roofing (tenting) of this doublet on a low-field spectrometer indicated that it was coupled to a signal within the aromatic envelope. This was confirmed by observing that the doublet signal at δ 5.91 collapsed to a singlet on irradiation at δ 7.18. The ^{1}H NMR spectrum of component **A** established that the unusual doublet signal which moved upfield to δ 5.66 at −50 °C (see below) is coupled to the triplet at δ 7.18 and forms part of a doublet–triplet–doublet system (Figure 2) assigned to the protons at the 2-, 3-, and 4-positions on the 1-naphthyl ring. An unambiguous assignment was obtained from selectively decoupled 67.8 MHz ^{13}C NMR spectra recorded at ambient temperature. Selective irradiation of the proton doublet at δ 5.91 was observed to remove a 4.0 Hz coupling from the ^{13}C=N multiplet (a doublet of quintets) of the major component **A** leaving a quintet signal (*J* 6.5 Hz). The residual quintet splitting arises from a two-bond ^{13}C,H coupling to the imino methyl protons, together with a three-bond coupling of a similar size (6.5 Hz) to the NCH proton. The removal of the 4.0 Hz ^{13}C,H coupling by irradiation of the proton doublet at δ 5.91 clearly identifies the latter resonance as belonging to the proton on the 2-position of the 1-naphthyl ring since only this proton would be expected to show a three-bond coupling of *ca.* 4 Hz to the imino carbon.

Clearly this proton signal is shifted far upfield of the normal resonance position of naphthalene ring β-protons, δ 7.5. The upfield shift, *ca.* 1.6 ppm is so large that the only viable explanation that can be advanced is a strong shielding effect from an adjacent π-electron circulation (aromatic ring current). The *N*-1-phenyl-2-propyl moiety is the only possible origin of such an effect, though there does not appear to be any evident reason as to why the phenyl moiety should lie close to the naphthyl proton at the 2-position. Since the low temperature dissolution experiment (see above) established that the crystals (isolated from a pentane solution) were composed of the major isomer **A** which was associated with the anomalous naphthyl proton resonance, it was considered worthwhile to investigate the crystalline material by X-ray crystallography.

The resulting structure and the crystallographic numbering scheme used is shown in Figure 4. The atomic co-ordinates are given in Table 1 and the bond lengths, bond angles, and selected torsion angles are listed in Table 2. The absolute configuration at C(13) is (*R*), established by the synthesis of the material from *R*-(+)-amphetamine. The X-ray analysis establishes that the major isomer (**A**) is the *Z*-atropisomer (**1a**). The torsion angles about C(1)–C(11), C(11)–N(1), N(1)–C(13), C(13)–C(15), and C(15)–C(16) which define the overall conformation of the molecule are listed in Table 2. The torsion angle at the imino double bond, C(1)–C(11)=N(1)–C(13), which is −4.0° establishes the *Z*-configuration. The naphthalene residue is oriented nearly perpendicular to the essentially planar C(1)–C(11)[C(12)]=N(1)–C(13) moiety with the naphthyl B ring directed *anti* to the amphetamine benzyl group (Figure 4). The two aromatic residues are each planar to within 0.01 Å, and the angle between them is 48.2°.

Bond lengths are generally normal and mostly agree with expected values to within the limits of experimental error. In the naphthalene residue, however, the C(1)–C(2) and C(6)–C(7) bond lengths are *ca.* 0.05 Å shorter than those found in the crystal structure of naphthalene itself,[8,9] while the adjacent C(2)–C(3) and C(7)–C(8) lengths are *ca.* 0.05 Å longer than in naphthalene. The naphthalene residue, therefore, while maintaining approximate 2/*m* (C_{2h}) symmetry, has lost the higher *mmm* (D_{2h}) symmetry[8,9] of naphthalene itself. MNDO molecular orbital calculations[10] on the title compound in which, starting from the X-ray structure, all the parameters of the naphthalene residue were optimized, resulted in a geometry virtually identical with that of the naphthalene molecule with approximate *mmm* symmetry. The statistically highly significant deviation of these bond lengths from the naphthalene values may, therefore, arise from some subtle electronic or steric effect, to which the MNDO approximation is not sensitive. However, the possibility that these anomalous bond lengths are merely the result of random errors in the structure analysis cannot be entirely ruled out (despite their apparent statistical significance), although in view of the otherwise normal bonding geometry, this seems unlikely.

Table 2. Bond lengths Å and bond angles ° with esds in parentheses and selected torsion angles esds *ca.* 0.7°.

Bond lengths

N–C(11)	1.266(6)	C(8)–C(9)	1.351(7)
N–C(13)	1.458(6)	C(9)–C(10)	1.411(7)
C(1)–C(2)	1.387(7)	C(11)–C(12)	1.506(7)
C(1)–C(10)	1.361(7)	C(13)–C(14)	1.511(7)
C(1)–C(11)	1.533(7)	C(13)–C(15)	1.532(7)
C(2)–C(3)	1.486(7)	C(15)–C(16)	1.498(8)
C(2)–C(7)	1.406(7)	C(16)–C(17)	1.385(8)
C(3)–C(4)	1.364(8)	C(16)–C(21)	1.405(9)
C(4)–C(5)	1.415(9)	C(17)–C(18)	1.370(10)
C(5)–C(6)	1.387(10)	C(18)–C(19)	1.351(11)
C(6)–C(7)	1.374(7)	C(19)–C(20)	1.381(11)
C(7)–C(8)	1.476(7)	C(20)–C(21)	1.389(9)

Bond angles

C(11)–N–C(13)	120.7(5)	C(1)–C(10)–C(9)	122.7(6)
C(2)–C(1)–C(10)	117.5(5)	N–C(11)–C(1)	127.5(5)
C(2)–C(1)–C(11)	118.9(5)	N–C(11)–C(12)	118.7(5)
C(10)–C(1)–C(11)	123.5(5)	C(1)–C(11)–C(12)	113.2(4)
C(1)–C(2)–C(3)	120.2(5)	N–C(13)–C(14)	108.9(5)
C(1)–C(2)–C(7)	122.8(5)	N–C(13)–C(15)	107.7(4)
C(3)–C(2)–C(7)	117.0(5)	C(14)–C(13)–C(15)	111.7(5)
C(2)–C(3)–C(4)	119.1(6)	C(13)–C(15)–C(16)	113.4(4)
C(3)–C(4)–C(5)	120.3(7)	C(15)–C(16)–C(17)	121.0(7)
C(4)–C(5)–C(6)	122.2(7)	C(15)–C(16)–C(21)	121.1(6)
C(5)–C(6)–C(7)	118.1(8)	C(17)–C(16)–C(21)	117.8(7)
C(2)–C(7)–C(6)	123.4(7)	C(16)–C(17)–C(18)	121.5(9)
C(2)–C(7)–C(8)	117.7(5)	C(17)–C(18)–C(19)	120.2(10)
C(6)–C(7)–C(8)	119.0(6)	C(18)–C(19)–C(20)	120.8(10)
C(7)–C(8)–C(9)	118.0(5)	C(19)–C(20)–C(21)	119.5(9)
C(8)–C(9)–C(10)	121.2(5)	C(16)–C(21)–C(20)	120.1(8)

Torsion angles

C(10)–C(1)–C(11)–N	−95.8
C(2)–C(1)–C(11)–N	87.3
C(10)–C(1)–C(11)–C(12)	75.6
C(1)–C(11)–N–C(13)	−4.0
C(12)–C(11)–N–C(13)	−175.0
C(11)–N–C(13)–C(15)	115.8
C(11)–N–C(13)–C(14)	−122.9
N–C(13)–C(15)–C(16)	−64.4
C(14)–C(13)–C(15)–C(16)	176.0
C(13)–C(15)–C(16)–C(17)	86.5
C(13)–C(15)–C(16)–C(21)	−90.8

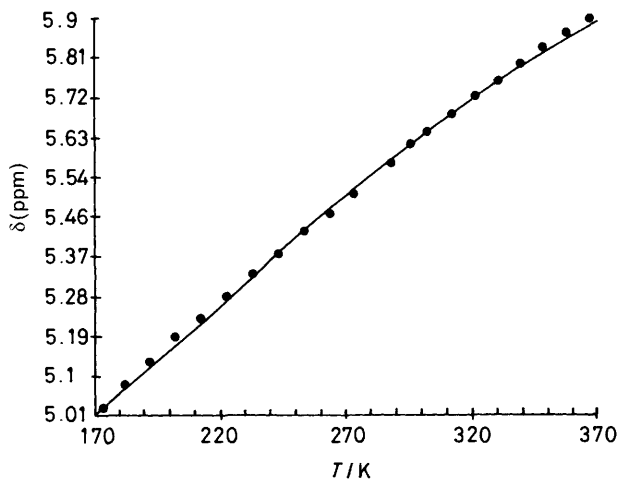


Figure 5. Plot of observed δ values (solid circles) in iso-octane and calculated δ values (solid line) for C(10)–H *vs.* temperature/K.

The most interesting feature of the crystal structure is that the aromatic hydrogen atom attached to the 2-position of the 1-naphthyl ring [C(10)–H using the crystallographic numbering system in Figure 4] is situated very close to the face of the amphetamine phenyl ring. Specifically this proton in its calculated position, assuming C–H = 1.08 Å, lies 2.68 Å above the plane of the amphetamine phenyl ring and the normal to this plane is displaced only 0.37 Å from the centre of the phenyl ring. Insertion of these measurements into the Johnson–Bovey ring-current equations[11] gives a predicted upfield shift for C(10)–H of 2.31 ppm due to the diamagnetic π-electron circulation. Subtraction of this shift from the normal resonance position of naphthalene β-protons (δ 7.5) results in a predicted δ value of 5.2 for C(10)–H. This compares with the observed δ value of 5.91 in deuteriochloroform at ambient temperature.

However, the chemical shift of this resonance was found to be unusually temperature dependent, moving upfield on lowering the temperature (δ 5.66 at −50 °C in deuteriochloroform compared with δ 5.91 at 20 °C). Iso-octane was selected as the solvent for a more detailed variable temperature study owing to the wide gap between its freezing and boiling points, and its non-polar, weakly solvating, nature. The plot of the C(10)–H signal position *vs.* temperature (Figure 5) departs only slightly from linearity over the range studied (−100 to +95 °C). At −100 °C this signal had moved further upfield to δ 5.0, which corresponds with the predicted chemical shift given by the Johnson–Bovey ring current calculations based on the X-ray conformation. However, it is clear from the plot in Figure 4 that even lower δ values would be obtained at lower temperatures. Attempts to obtain δ values for C(10)–H above 100 °C (in decalin) were thwarted by signal collapse due to the onset of fast site-exchange between this signal and another signal located in the aromatic envelope. Above 100 °C the atropisomers (**1a**) and (**1b**) interconvert rapidly on the NMR time-scale by rotation about the naphthyl–imine bond.

The marked temperature dependence of the chemical shift of C(10)–H in isomer (**1a**) can be rationalized in terms of an equilibrium in solution between two molecular conformations of atropisomer (**1a**); one approximating to the conformation (**I**) existing in the solid state (Figure 4), and another (**II**) where the amphetamine phenyl ring is much further away from C(10)–H which therefore has no ring current shielding (Scheme). Conformations (**I**) and (**II**) interconvert rapidly on the NMR time-scale at all accessible temperatures.

$$\text{Conformation (I)} \overset{K}{\rightleftharpoons} \text{Conformation (II)}$$

C(10)–H shift: δ_I δ_{II}
Fractional population: P_I $(1 - P_I)$

$$K = (1 - P_I)/P_I = \exp[(T\Delta S^\circ - \Delta H^\circ)/RT] \quad (1)$$

$$\text{Observed } \delta = P_I\delta_I + (1 - P_I)\delta_{II} \quad (2)$$

Computer fitting (Figure 5) of the observed δ *vs.* T plot (in iso-octane) gave:

$$\Delta S^\circ = 2.77 \text{ cal mol}^{-1} \text{ K}^{-1} *$$

$$\Delta H^\circ = 1\,305 \text{ cal mol}^{-1}$$

where δ_I = 4.8 ppm, δ_{II} = 7.5 ppm.

Scheme.

* 1 cal = 4.184 J.

An interactive computer program was used to generate δ *vs.* temperature curves according to equations (1) and (2) in the Scheme from various values of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, δ_I and δ_{II}. The optimum agreement between calculated and experimental plots, depicted in Figure 5, was obtained with the values given in the Scheme. The optimized value of δ_I (4.8) is very close to the chemical shift of C(10)–H (δ 5.2) given by the Johnson–Bovey ring current calculations on the solid state conformation. The chemical shift of C(10)–H in the second proposed conformer gave a satisfactory fit at δ_{II} 7.5 which is the normal signal position for a naphthalene β-hydrogen.

It is clear from the thermodynamic parameters in the Scheme that the solid state conformation (**I**) is energetically favoured in solution and hence becomes more populated at lower temperature causing the observed upfield movement of C(10)–H with decreasing temperature. The entropy term on the other hand favours conformation (**II**) which therefore becomes increasingly populated at high temperatures. It is reassuring that the estimated value of $\Delta S^{\ddagger}$ (2.8 cal mol^{-1} K^{-1}) is of a reasonable magnitude for a conformational equilibrium. Furthermore the lower entropy of the solid-state conformer (**I**) is in line with expectations as this conformer is quite sterically hindered due to the close proximity of the naphthyl ring and the benzyl group. Although the precise geometry of the proposed second solution conformation (**II**) is unknown it is almost certainly less sterically congested than conformation (**I**).

It is interesting to consider why isomer (**1a**) favours, on an enthalpy basis, a hindered conformation (**I**) where the naphthyl ring is in close proximity to the amphetamine phenyl moiety and almost orthogonal to the imino plane. It seems unlikely that this conformation is forced on the system by even greater steric repulsions in all alternative conformations. Indeed, an inspection of molecular models indicates several other less congested conformations available to (**1a**), resulting from rotation about the N–CH and CH–CH_2Ph bonds. The proposed second conformation (**II**), which becomes increasingly populated in solution at higher temperatures, is evidently one of these possibilities.

Accordingly, it seems likely that the congested conformation (**I**) is energetically favoured due to a weak attractive interaction between the naphthyl and phenyl rings. This view is supported by the fact that conformation (**I**) is energetically favoured in the *Z*-form atropisomer (**1a**) which is itself favoured over both the other atropisomer (**1b**) and the *E*-isomer (**1c**).

Regarding the nature of the possible attractive interaction in (**1a**), it is clearly not a classical face-to-face charge transfer π-complex as the naphthyl and phenyl rings are mutually inclined at an angle of 48°. The X-ray and NMR results suggest that there may be a weak attractive interaction of some sort between the naphthyl C(10)–H and the π-electrons of the neighbouring phenyl ring. Attractive 'edge-to-face' interactions between two aromatic rings have recently been proposed in other systems.[12–16] Both intramolecular[12,13] and intermolecular[14] attractive interactions have been discussed. Usually the aromatic hydrogen is found to lie 2.8–2.9 Å above the centroid of a second aryl residue (*c.f.* 2.7 Å in the present case). *ab initio* Molecular orbital calculations[15,16] on model interactions, involving aromatic acid side chains, have led to the suggestion that the edge-to-face effect lowers the enthalpy by 1–2.5 kcal mol^{-1}. The variable temperature n.m.r. results (Scheme) suggest that the attractive edge-to-face interaction in (**1a**) may be worth *ca.* 1.3 kcal mol^{-1} in enthalpy terms, *i.e.* within the range estimated by theoretical calculations.

* For details of the CCDC deposition scheme, see 'Instructions for Authors,' (1990) *J. Chem. Soc., Perkin Trans. 2*, 1990, issue 1.

Experimental

NMR spectra were recorded on JEOL GX-270 and FX-90Q spectrometers. Variable temperature n.m.r. studies were performed on the latter instrument, and probe temperatures were measured using a digital copper-constantan thermocouple with the lead inserted into a sample tube at the level of the coil.

Theoretical δ *vs.* temperature curves were generated from equations (1) and (2) (Scheme) using a BASIC program running on an Amstrad PCW9512 micro computer equipped with a Radio Shack graphic printer.

N-[1-(1′-*Naphthyl*)*ethylidene*]-1-*phenyl*-2-*propylamine* (**1**).—This imine was obtained in 83% yield by heating under reflux, in a Dean–Stark apparatus, an equimolar mixture of 1-(1′-naphthyl)ethanone and *R*-(+)-1-phenyl-2-propylamine [(+)-amphetamine] in toluene containing a trace of toluene-*p*-sulphonic acid. Recrystallization from pentane afforded colourless crystals, m.p. 97–98 °C, $[\alpha]_D$ −34.5° ($CHCl_3$) (Found: C, 87.6; H, 7.3; N, 5.0. $C_{21}H_{21}N$ requires C, 87.8; H, 7.3; N, 4.9%); ν_{max} 1 640 cm^{-1} (C=N); δ_H(90 MHz; $CDCl_3$) 1.05 [d, CH*Me*, (**1b**)] 1.11 [d, CH*Me*, (**1a**)], 1.38 [d, CH*Me*, (**1c**)] 2.00 [s, =CMe, (**1c**)], 2.30 [s, =CMe, (**1a**)], 2.33 [s, =CMe, (**1b**)], 2.6–3.0 [m, CH_2, (**1a–c**)], 3.17 [m, NCH, (**1a**) and (**1b**)], 4.11 [m, NCH, (**1c**)], 5.91 [d, C(10)–H, (**1a**)], 6.8–7.9 [m, ArH, (**1a–c**)]. δ_C(67.8 MHz; $CDCl_3$) 19.85 [=C*Me*, (**1c**)], 21.67 [CH*Me*, (**1b**)], 21.94 [CH*Me*, (**1a**) and (**1c**)], 29.18 [=C*Me*, (**1a**)], 29.34 [=C*Me*, (**1b**)], 44.50 [CH_2, (**1c**)], 44.69 [CH_2, (**1b**)], 44.73 [CH_2, (**1a**)], 58.16 [CH, (**1c**)], 59.65 [CH, (**1b**)], 59.73 [CH, (**1a**)], 122.7–141.7 (numerous aromatic signals), 166.31 [C=N, (**1c**)], 166.66 [C=N, (**1a**)], 167.08 [C=N, (**1b**)].

X-Ray Structural Analysis and Refinement.—A crystal (0.4 × 0.4 × 0.6 mm) of imine (**1**) was mounted on an Enraf–Nonius CAD-4 diffractometer; cell dimensions and intensities were measured by ω/2θ scans with graphite-monochromated Mo-K_α radiation and scan range $\omega = (1.0 + 0.35 \tan\theta)°$.

Scan speed varied from 1.8 to 5.0° min^{-1} depending on the intensity. 2 568 reflections were scanned within $2 < \theta < 26°$. Of these 2 370 were unique (merging $R_{int} = 0.018$) (Friedel pairs not merged). Two standard reflections measured every 2 h showed no significant variation in intensity. 1 474 structure amplitudes with $F > 5\sigma(F)$ were considered observed and used in the analysis.

Crystal Data.—$C_{21}H_{21}N$, $M = 287.4$, orthorhombic, $P2_12_12_1$, $a = 7.821(1)$, $b = 14.408(4)$, $c = 15.104(11)$ Å, $V = 1\,702.0$ Å, $Z = 4$, $D_c = 1.122$ g cm^{-3}, $F(000) = 616$, μ(Mo-K_α) = 0.060 mm^{-1}, $\lambda = 0.710\,69$ Å.

The structure was determined by direct methods and refined by least squares using anisotropic thermal parameters for the heavier atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms. Isotropic temperature factors were refined for the hydrogen atoms. Unit weights, which resulted in a satisfactory weighting analysis, were used in the least-squares refinement. The refinement converged to $R = 0.059$, with a maximum shift/error ratio of 0.09. The residual electron density in a final difference map was within the range −0.19 to 0.37 e $Å^{-3}$. The inverse structure gave identical *R*.

Complex neutral-atom scattering factors were employed. Computations were carried out on the University of Birmingham Honeywell computer and at the University of Manchester Regional Computer Centre with the SHELX86,[17] SHELX76,[18] and PLUTO[19] programs.

Lists of anisotropic thermal parameters and hydrogen atom co-ordinates for (**1**) have been deposited at the Cambridge Crystallographic Data Centre.*

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